

Synthesis of Aragonite Superstructure from Steelmaking Slag via Indirect CO₂ Mineral Sequestration

WeiJun Bao, Huiquan Li

Abstract—Using steelmaking slag as a raw material, aragonite superstructure product had been synthesized via an indirect CO₂ mineral sequestration route. It mainly involved two separate steps, in which the element of calcium is first selectively leached from steelmaking slag by a novel leaching media consisting of organic solvent Tributyl phosphate (TBP), acetic acid, and ultra-purity water, followed by enhanced carbonation in a separate step for aragonite superstructure production as well as efficiency recovery of leaching media. Based on the different leaching medium employed in the steelmaking slag leaching process, two typical products were collected from the enhanced carbonation step. The products were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM), respectively. It reveals that the needle-like aragonite crystals self-organized into aragonite superstructure particles including aragonite microspheres as well as dumbbell-like spherical particles, can be obtained from the steelmaking slag with the purity over 99%.

Keywords—Aragonite superstructure, Steelmaking slag, Indirect CO₂ mineral sequestration, Selective leaching, Enhanced carbonation.

I. INTRODUCTION

STEEL manufacturing is one of the biggest industries over the world. It not only produced worldwide more than one billion metric tons of steel annually, but also by-produced large plenty of slag [1]. Most of the steel is manufactured from an using the traditional route, in which iron is first reduced to molten iron using coke as reducing agent, and then poured into the basic oxygen furnace to burn off the carbon in the molten iron, and finally producing low carbon steel. In order to remove impurities from molten iron and crude steel, limestone or burnt lime is added for the formation of slag. It is estimated that the value of steelmaking slag produced from basic oxygen furnace is about 0.15-0.20 t slag per ton steel [2]. Although steelmaking slag can be used as a substitute for gravel in road construction or lime in agriculture, specifically in China, its utilization ratio is limited to about 36% because of the high alkaline-earth metal (e.g., Ca and Mg) oxide content in this slag, indicating that heavy metal elements are released into the environment [3]. For a ten-million-ton grade integrated iron and steel enterprise in China, the annual amount of steelmaking slag produced is about

1 Mt, while more than 800 kiloton steelmaking slag is remain treated as landfill[4]. Therefore, one of the urgent problems is to seek a new utilization option for cheap and readily available steelmaking slag.

Calcium carbonate (CaCO₃), an important inorganic material, has various industrial applications as a filler in paper, rubber, plastics, paints and so on [5, 6]. CaCO₃ has three kinds of crystal polymorphs, namely calcite, aragonite, and vaterite, with rhombohedral, orthorhombic, and hexagonal structures, respectively [7, 8]. The application of calcium carbonate particles is determined by a number of strictly defined parameters, such as morphology, structure, size, specific surface area, brightness, oil adsorption, chemical purity, and so on [9]. The needle-like aragonite crystal with high aspect ratios has been in great demand for the improvement of mechanical properties of polymer materials [10, 11], while it is slightly less stable under similar conditions and is eventually transformed to calcite [12]. Many researchers have been concentrating on the synthesis of needle-like CaCO₃ crystals. Tanaka et al. [13] had synthesized needle-like aragonite by reaction of the milk of lime-containing aragonite seed crystal with CO₂-containing gas. However, the reaction must be regulated within pH 8–9 by careful addition of CO₂-containing gas to obtain the needle-like aragonite. Chakrabarty et al. [14] and Wang et al. [15] had reported a novel and easy approach for the synthesis of aragonite crystal with unconventional morphologies via double decomposition of an aqueous solution of CaCl₂ and Na₂CO₃ without any additive or in the presence of a suitable surfactant, respectively. Most of the raw materials for aragonite crystal synthesis are based on the pure chemicals, while there is little report on the aragonite produced from industry solid waste.

CO₂ mineral sequestration, a promising alternative sequestration route, has been widely studied in recent years. The basic concept behind mineral CO₂ sequestration is to mimic natural weathering processed in which calcium or magnesium silicates are transformed into carbonates [16]. The process of CO₂ mineral sequestration can be distinguished into direct routes in which the mineral material is carbonated in one step, and indirect routes in which the reactive components are first extracted from the mineral matrix by recycling medium and then carbonated in a separate step [17]. The indirect CO₂ mineral sequestration currently becomes the most attractive route, particularly as either the dissolution step or the subsequent precipitation step, or both, can potentially be developed for large-scale applications with economic efficiency [18]. A

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possible feedstock for mineral CO₂ sequestration, which has attained much attention so far, is industry solid waste, such as steelmaking slag, and so on. These materials are generally alkaline and rich in calcium. The major advantages compared to ores are their low costs, the widespread availability in industrial areas and their chemical instability shown more reactive than primary minerals [19]. Moreover, the industry solid waste also contains abundant metal elements, which can be recovered for further industrial application. Therefore, it is a good idea for reducing CO₂ emission from an integrated iron & steelmaking enterprise by indirect CO₂ mineral sequestration using steelmaking slag as raw materials.

In this work, a new process for large scale synthesis of needle-like aragonite from steelmaking slag via indirect CO₂ mineral sequestration has been proposed. It mainly involved two separate steps, in which the reactive components are first extracted from the steelmaking slag by a novel leaching media consisting of organic solvent Tributyl phosphate (TBP), acetic acid, and ultra-purity water, followed by enhanced carbonation in a separate step for fixation of CO₂ into a value-added as well as efficiency recovery of leaching media. The optimal conditions both for leaching of steelmaking slag and for carbonation steps had been experimental investigated. The obtained product was characterized by XRD, SEM, and it displayed wide application prospects and relatively high value.

II. MATERIALS AND METHODS

A. Materials

Steelmaking slag was collected from the steel production process using a 120 t basic oxygen furnace by Jinan Iron & Steel Integrated Co. The slag was dried at 60 °C in an oven and crushed at a particle size smaller than 50 mesh for all of the following experimental runs. The XRD analysis of the used steelmaking slag showed that it consisted of lime(CaO), calcium hydroxide (Ca(OH)₂), calcium carbonate (CaCO₃), calcium fluoride (CaF₂), quartz (SiO₂), magnesium hydroxide (Mg(OH)₂), wuestite (FeO), calcium iron oxide (Ca₂Fe₂O₅), and larnite (Ca₂SiO₄) with less amount of akermanite (Ca₂MgSi₂O₇). The chemical composition of the used steelmaking slag was listed in Table 1, which was measured by ICP-AES respectively. According to the ICP-AES analyses, the Ca, Mg, Fe, Al, and Si content in the prepared steel-making slag was high, which indicated it was not suitable for building material but had a potential application for mineral CO₂ sequestration as well as high value-added calcium carbonate production.

TABLE I
COMPOSITION OF THE SELECTED ELEMENTS IN THE PREPARED STEELMAKING
SLAG AS DETERMINED BY ICP-AES ANALYSIS

Element	Ca	Mg	Fe	Al	Si
wt %	25.60	6.96	11.16	3.43	8.47

The reaction medium used in the steelmaking slag leaching step was a composite of a water phase and an organic phase. The

water phase used only ultra-pure water; while the organic phase was prepared by first completely mixing the glacial acetic acid, TBP, and ultra-pure water in a stirring container and, then, finally taking the upper organic solvent phase after it was left standing for a few minutes; Therefore, the quantity of the added acetic acid can be determined by both the volume of the organic phase and the initial concentration of acetic acid in the organic phase. Herein, glacial acetic acid (HAc, 99.8 wt %) and TBP (TBP, 98.5 wt %) were of analytical grade, which were purchased from Beijing Chemical Reagent Co., and used as received without further purification.

The leached solution from steelmaking slag was directly employed for carbonation step. The CO₂ gas of 99.99% purity used in carbonation step, was purchased from Beijing Ap Beifen Gases Industry Company Limited.

B. Apparatus

The steelmaking slag leaching step was conducted in a three-mouth flask with a temperature monitor and a sampling port. The reactor of the three-mouth flask with a volume of 1 L was surrounded by a temperature-controlled water bath. The leaching medium in this reactor was stirred using a mechanical stirrer.

The second carbonation step was conducted in a high-pressure stainless steel 500 ml reactor that had a maximum bearing-pressure of 24 MPa. The reactor had an entry pipe for CO₂ gas addition and an exit pipe for product discharge. The CO₂ gas was dispersed through the reactor by means of a three-bladed pitched turbine. A man-made filter was connected to the outer pipe to separate out the calcium carbonate solids from the mixed aqueous solution at high pressure conditions.

C. Procedure

The procedure of synthesis aragonite superstructure from steelmaking slag is mainly composed of two key steps, as shown in Figure 1. In steelmaking slag leaching step, the leaching medium which involved the organic phase mixed with a certain volume of ultra-pure water, was added to the reactor at the beginning of the experiment and then stirred at a certain speed. The water bath was then heated to a constant temperature. When the monitored temperature in the reactor reached the setting temperature value, the prepared slag was added to the reactor and reaction time was recorded. After some time, stirring was stopped and the residual slag was removed from the solution through sedimentation and filtration. The filtrate delaminated quickly, and the superstratum was sampled to determine the residual acetic acid concentration. The underlayer of the filtrate was separated and then mixed to a fixed volume with the lotion from the residual slag and ultrapurity water for analysis. After analysis, the filtrate with equivalent volume of the superstratum and the underlayer, was introduced into the reactor under atmospheric pressure in carbonation step. The reactor was then heated to a constant temperature and the CO₂ gas was introduced into the reactor from a CO₂ gas cylinder. Once the air in the reactor was displaced, the CO₂ gas was allowed to flow until it reached the setting pressure, and a timed reaction was

initiated. Throughout the experiment, the CO_2 pressure in the reactor was kept constant by regulation of the supply of CO_2 from the cylinder with a pressure controller. After a specified time, the stirring was stopped, the entire system was vented, and the reaction contents were quickly filtered through the man-made filter. All of the deposited CaCO_3 was collected and washed several times with deionized water, followed by anhydrous ethanol, then dried in an oven at 105°C for 12 hours. The filtrate delaminated quickly, and the superstratum was sampled for analysis. After that, the obtained filtrate from carbonation step was directly recycled to steelmaking slag leaching step. Therefore, more aragonite superstructure particles were produced from steelmaking slag.

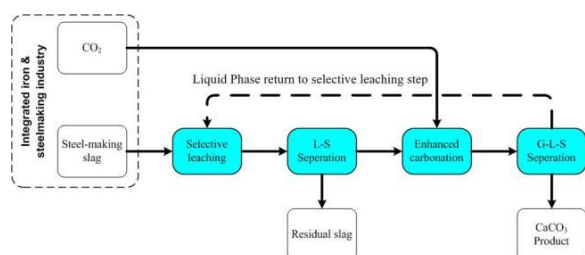


Fig. 1 Simplified schematic diagram of aragonite superstructure produced from steelmaking slag.

D. Characteristic

The composition of the steelmaking slag was analyzed using X-ray diffraction (XRD) (X'pert Pro MPD X-ray diffractometer from PANalytical). The contents of Ca, Mg, Fe, Al, and Si in steelmaking slag as well as in steelmaking leaching solution, were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (OPTIMA 5300DV inductively coupled plasma-optical emission spectrometry manufactured by Perkin-Elmer, USA). The aragonite superstructure particles were weighed with an analytical balance and also examined by Powder X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) (JSM 6700F NT, Japan). The acetic acid concentration in the organic phase was titrated against a standard NaOH solution using anhydrous ethanol as a diluent.

III. RESULTS AND DISCUSSION

A. Selective leaching of steelmaking slag

In the steelmaking slag leaching process, a mixture of organic solvent TBP, acetic acid, and ultra-pure water, was employed as leaching medium. Prior to reaction, the acetic acid only existed in the organic phase, showing a formation of (1:1) acid-extractant complexes with TBP [20, 21]. When this organic phase contacted with the water phase, the acetic acid was partially stripped and then transformed from the organic phase into the water phase. Therefore, the leaching medium that reacted with steelmaking slag was mainly the acetic acid in the water phase reacting with the steelmaking slag. Based on the elements in the prepared steel-making slag as determined by ICP-AES analysis, the contents of Ca, Mg, Fe, Al, and Si were

leached from the steelmaking slag. And an increase in both the leaching rate of calcium and the extraction rate of magnesium can be observed with high acidity; meanwhile, aluminum, iron, and silica are dissolved in large quantities. Moreover, the dissolved magnesium, aluminum, iron, and silica would greatly affect on the calcium carbonate production in carbonation step. In fact, the existed magnesium in leaching solution could hardly be carbonated under the same condition of calcium carbonate production. Therefore, large quantities of calcium and magnesium except other elements dissolved from the steelmaking slag, was preferred during leaching step.

A number of variables affected the leaching behavior of Ca, Mg, Fe, Al, and Si from steel-making slag by the leaching media involving organic solvent TBP, acetic acid and ultra-purity water. These variables are including stirring speed, phase volume ratio, organic solvent to solid ratio, the initial acetic acid concentration, acid to slag ratio, reaction temperature and reaction time. Among them, the acid to slag ratio means the mass ratio between the added acetic acid and the slag at the initial reaction time. In this study, the steelmaking slag leaching experiments were conducted under the conditions of stirring speed 500 rpm, phase volume ratio 1, organic solvent to solid ratio 10, the initial acetic acid concentration 1.25 mol/L, acid to slag ratio 0.75, reaction temperature 94°C . During the leaching reaction, samples were taken from the mixed solution at 2, 5, 10, 20, 30, 40, 50, and 60 min after reaction. The residual acetic acid concentration in organic phase and the concentrations of the main elements from the slag (e.g., calcium (Ca), magnesium (Mg), iron (Fe), aluminum (Al), and silicon (Si)) were determined by ICP-AES, as shown in Figure 2.

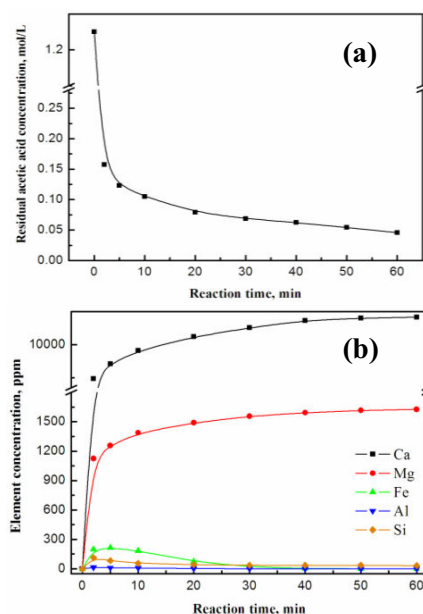


Fig. 2 Effect of reaction time on (a) residual acetic acid concentration in the organic phase; (b) leaching of Ca, Mg, Fe, Al and Si from steelmaking slag.

Figure 2a shows that the residual acetic acid concentration in

the organic phase decreased with the increase of the reaction time, and it decreased rapidly during the first 5 min. After 60 min reaction time, more than 96% of acetic acid was converted into acetate. Figure 2b shows the concentration of Ca, Mg, Fe, Al, and Si in the leaching aqueous solution at different reaction time. As shown in Figure 2b, the concentration of leached Ca and Mg increased with the reaction time. It increased rapidly in the first 5 min, and its growth rate decreased when the reaction time was extended to 60 min. However, the concentration of leached Fe reached a peak value in the first 5 min, and then decreased rapidly with the increase of the reaction time. The leached Fe could hardly be detected after 60 min of reaction. The concentrations of leached Al and Si displayed a similar tendency at different reaction times. They increased to a peak value and then decreased with the increase of the reaction time, and they were hardly detected after only 30 min of reaction. It can be concluded that the element of Ca and Mg from steelmaking slag could be selectively leached by the novel leaching media consisting of organic solvent Tributyl phosphate (TBP), acetic acid, and ultra-purity water. And the leaching ratios of Ca and Mg were reached 75% and 35% after 60 min of reaction, respectively.

B. Enhanced carbonation for carbonate production

The possible occurred reactions in steelmaking slag selective leaching solution carbonation step are mainly involving the reaction between CO_2 and calcium acetate and the reaction between CO_2 and magnesium acetate in aqueous solution. The former was firstly proposed by Kakizawa et al. [22], based on the fundamental that the dissociation constant pK_a of carbonic acid (3.6 at 298 K) is smaller than the acetic acid (4.76 at 298 K), under the condition of high CO_2 pressure. The acetic acid would be replaced by carbonic acid in such a carbonation crystallization process, and then results in precipitating CaCO_3 particles. The latter was also investigated by Teir et al. [23], based on the thermodynamic equilibrium calculation that the reaction can occur spontaneously at temperatures above 144 °C at atmospheric pressure. However, both the reactions were limited by the low crystallization conversion. For one thing, as investigated by Kakizawa et al. [22], the deposited CaCO_3 particles which produced from the reaction between CO_2 and calcium acetate in aqueous solution, can be re-dissolved by the generated acetic acid with the increase of reaction time and CO_2 partial pressure. For another thing, the exploratory experiment result shows that no solid product can be deposited from the reaction between CO_2 and magnesium acetate in aqueous solution, under the condition that the concentration of magnesium acetate 1.5 mol/l, reaction time 60 minutes, stirring speed 500 rpm, reaction temperature 80 °C, CO_2 partial pressure 4.0 MPa. Consequently, with the low carbonation efficiency of this carbonation step, more leached solution has to be recycled, which resulted in consuming more energy for calcium carbonate production and deteriorating the whole process economic efficiency. Therefore, large quantities of calcium from steelmaking slag leaching solution could be converted into calcium carbonate and high crystallization conversion could be

reached as well, was preferred during carbonation step.

In order to enhance the carbonation reaction in this step, we had tried to introduce tributyl phosphate (TBP) to the reaction mixture, which could react with acetic acid to form a reversible chemical complex [24]. The acetic acid would now be transferred from the aqueous phase to the organic phase by complexing with TBP, allowing an improved crystallization conversion. It is interesting that the enhanced carbonation reaction conditions were achieved after selective leaching of steelmaking slag by the leaching media involving organic solvent TBP, acetic acid and ultra-purity water. Several variables, including stirring speed, phase ratio, reaction time, reaction temperature, CO_2 partial pressure and the concentration as well as the pH value of initial aqueous solution, had greatly affected on this enhanced carbonation process. In this paper, the effect of the reaction time on the enhanced calcium acetate carbonation process under the condition of initial calcium acetate concentration 1.52 mol/L, pH 7, phase ratio 1, CO_2 partial pressure 4.0 MPa, reaction temperature 80 °C, and stirring speed 500 rpm, was experimentally investigated, and the results were compared with the Kakizawa's report, as shown in Figure 3.

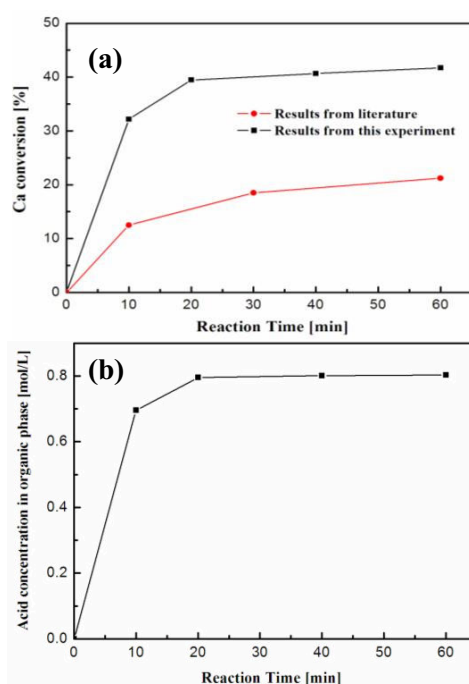


Fig. 3 Effect of reaction time on (a) crystallization conversion; (b) acetic acid concentration in organic TBP phase.

Figure 3a shows the crystallization conversion both obtained from our experiment and from Kakizawa's report increases with reaction time. From our experiment, the crystallization conversion increased quickly in the first 10 minutes and then more slowly increased over the next 10 minutes. When the reaction time exceeded 20 minutes, increases in crystallization conversion were only about 2.0% over the last 40 minutes.

However, the crystallization conversion in Kakizawa's report was always increased with the reaction time, while the growth rate decreased. With the reaction time of 20 minutes, the obtained crystallization conversion from our experiment was reached more than 40%, while the crystallization conversion reported by Kakizawa was less than 20%. Figure 3b shows the acetic acid concentration in organic TBP phase displayed a similar trend in changes with time, comparing to the crystallization conversion obtained from our experiment. The acetic acid concentration in organic TBP phase was increased with the reaction time, and it was reached about 0.8 mol/L when the reaction time exceeded 20 minutes. It can be concluded that with the addition of TBP, the produced acetic acid can further react with TBP to form (1:1) acid-extractant complexes, and they are extracted into organic phase, which leading to more solid calcium carbonate particles deposition. Therefore, the element of Ca after selective leached from steelmaking slag, can be greatly converted into calcium carbonate product by this enhanced carbonation step.

C. Product characteristics

Two typical products were collected from the enhanced carbonation step. One is the using of the steelmaking slag selective leaching solution as raw material, wherein the leaching medium employed in the steelmaking slag leaching process is composing of a mixture of organic solvent TBP, acetic acid, and ultra-pure water. The other is still using of the steelmaking slag selective leaching solution as raw material, but leaching medium employed in the steelmaking slag leaching process is the filtrate from former enhanced carbonation step. The operation conditions both for steelmaking slag selective leaching step and enhanced carbonation step are including: 1) stirring speed 500 rpm, phase volume ratio 1, organic solvent to solid ratio 10, the initial acetic acid concentration 1.25 mol/L, acid to slag ratio 0.75, reaction temperature 94 °C, and reaction time 60 min for the former step; 2) stirring speed 500 rpm, phase ratio 1, CO₂ partial pressure 4.0 MPa, reaction temperature 80 °C, pH 7, and reaction time 30 min for the latter step. Those two typical products were characterized by XRD and SEM, as shown in Figure 4 to Figure 6.

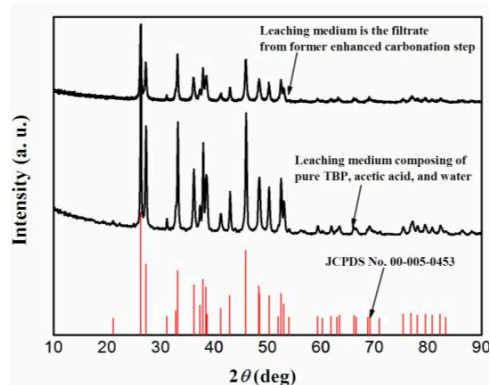


Fig. 4 XRD patterns of the two typical products obtained from steelmaking slag.

Figure 4 shows XRD patterns for the two typical solid products. The two typical solid products displayed almost the same XRD patterns. The XRD patterns of the sample indicates that the diffraction peaks are consistent with JCPDS Card No. 00-005-0453. The peaks with 2θ values of 21.10, 26.26, 27.24, 31.15, 33.16, 36.16, 37.32, 37.92, 38.45, 41.26, 42.96, 45.90, 48.32, 50.20, 52.47, and 53.10 can be correlated to the (hkl) indices (110), (111), (021), (002), (012), (200), (031), (112), (130), (211), (220), (221), (202), (132), (113), (231), respectively, of pure aragonite.

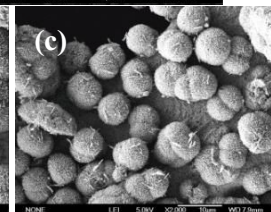
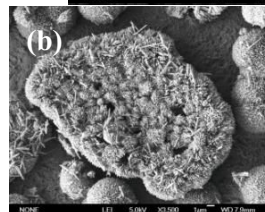
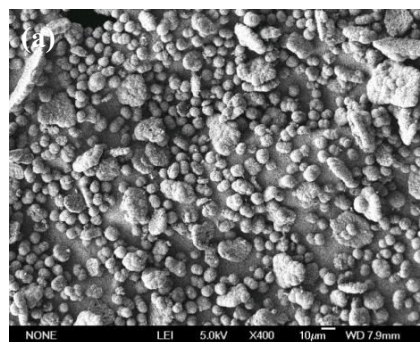


Fig. 5 SEM of the typical product obtained from steelmaking slag with leaching medium composed of pure TBP, acetic acid, and ultra-pure water: (a) an overview of the formed particles; (b) and (c) magnified views of the product.

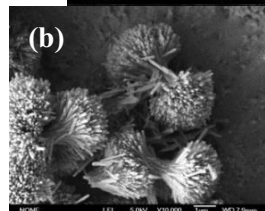
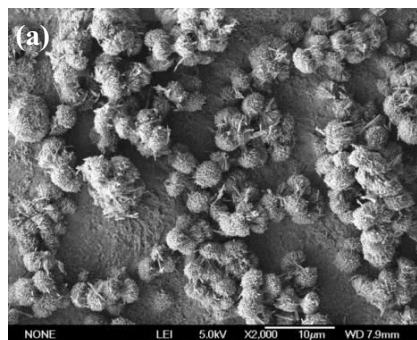


Fig. 6 SEM of the typical product obtained from steelmaking slag with employing filtrate from former enhanced carbonation step as leaching medium: (a) an overview of the formed particles; (b) and (c) magnified views of the product.

The morphology of the products was determined by SEM. Figure 5 shows the SEM image of the products obtained from steelmaking slag with the leaching medium composing of a mixture of organic solvent TBP, acetic acid, and ultra-pure water. The overview SEM micrograph of these typical solid particles was showed in Figure 5a. It can be seen that this typical product contains a small part of agglomerated massive particles and non-agglomerated calcium carbonate microspheres as well. The agglomerated massive particles with roughness surface, are composed of needle-like particles, and the particle diameter is about 40 μm , and thickness is 5 ~10 μm . However, the non-agglomerated calcium carbonate microspheres are also composed of needle-like particles, and the particle diameter is 5 ~10 μm . Figure 6 shows the EM image of the products obtained from steelmaking slag with the filtrate from former enhanced carbonation step used as the leaching medium. Compared to Figure 5, these typical solid particles have little agglomeration with the particle diameter of about 5 μm , which are also composed of some kinds of dumbbell-like spherical particles and needle-like crystallites, as shown in figure 6a. It reveals that the needle-like aragonite has self-organized into dumbbell-like spherical particles [25], as shown in figure 6b and figure 6c.

Moreover, the product was also dissolved by hydrochloric acid and analyse by ICP-AES to determine the content of Ca, Mg, Fe, Al, Si. The results showed that exception of Ca, no other element from steelmaking slag could be found in the aragonite superstructure particles, and the purity was over 99%. It also indicated that though the element of Mg could be leached from the steel-making slag, it could never be formed carbonate through this enhanced carbonation step. From its morphology, it can be concluded that the formed aragonite superstructure product would have wide application prospects and relatively high value in popular uses. This creates the favourable situation in which CO₂ greenhouse gas can be fixed into a value-added product.

IV. CONCLUSION

In this work, a new process of aragonite superstructure particles synthesis from steelmaking slag via indirect CO₂ mineral sequestration had been investigated. It mainly involved two separate steps, including selective leaching of steelmaking slag and enhanced carbonation for calcium carbonate production. By employing the novel leaching media consisting of organic solvent Tributyl phosphate (TBP), acetic acid, and ultra-purity water, only Ca and Mg could be leached with the leached ratios of 75% and 35% after 60 min of reaction, respectively. In the enhanced carbonation step, the element of Ca after selective leached from steelmaking slag, can be greatly converted into calcium carbonate product with the crystallization conversion reached above 40%. The solid product obtained from this new process with steelmaking slag as a raw material, was characterized as pure aragonite superstructure. It further reveals that the needle-like aragonite crystals have self-organized into aragonite microspheres as well as dumbbell-like spherical particles. The results of this

investigation are encouraging and give impetus for pursuing CO₂ sequestration by mineral carbonation.

ACKNOWLEDGMENT

The authors are grateful for the financial support of the National Natural Science Foundation of China (No.50974112), and the Major Program of National High Technology Research and Development Program of China (No.2011AA06A105).

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